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TAPPI, vol.65, no.4, April 1982, pp. 123-125, Atlanta, Georgia, US; A.J. SHARPE, Jr. et al.:"Improved cationic conductive polymer displays outstanding filmability"

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Description

This invention relates to a paper coating composition, a process for preparing a paper coating composition and a method for coating a paper with a paper coating composition. This invention also relates to a paper recycling process in which a coated paper of the invention is employed as "broke" in a paper making process. "Broke" is the term used in the art for paper, cardboard, or the like which is to be recycled.

Calcium carbonate is known as a paper coating pigment and, because it normally carries a positive charge, it is conventionally dispersed with an anionic dispersing agent. Other paper coating pigments which carry a neutral or positive charge exist, such as gypsum, talc, calcined kaolin clay, and these must also be dispersed using an anionic dispersing agent. (These minerals are also recognised as having a deficiency in negative sites).

A full discussion of the constituents of paper coating compositions and of the methods of applying such compositions to paper is given in Chapter XIX, Volume III of the second edition of the book by James P. Casey entitled "Pulp and Paper: Chemistry and Chemical Technology". A further discussion is given in "An Operator's Guide to Aqueous Coating for Paper and Board", edited by T.W.R. Dean, The British Paper and Board Industry Federation, London, 1979.

DE-A-3707221 and EP-A-0307795 disclose a cationic pigment dispersion. The pigment is first given a protective colloid cover using a cationised polymer and then, under certain circumstances, is dispersed with a cationic polymer.

TAPPI, vol. 65, no. 4, April 1982, pages 123-125, Atlanta, Georgia, U.S.A.; A.J. Sharpe, Jr. et al.: "Improved Cationic Conductive Polymer Displays Outstanding Filmability" describes a polysalt formed from the interaction of a strongly cationic polymer, such as a poly(diallyl dimethyl ammonium chloride), and a weakly anionic polymer, such as polyacrylic acid. The thus-formed polysalt is added in substantial quantities (of the order of 50% by weight, based on the weight of the pigment) to a predispersed, low solids pigment slurry in order to provide a conductive coating colour which is used to prepare a paper having a conductive surface.

According to a first aspect of the present invention there is provided an aqueous paper coating composition which comprises (i) at least 45% by weight of a particulate inorganic pigment dispersed with a dispersing agent and (ii) an adhesive; characterised in that said dispersing agent comprises an anionic polyelectrolyte and a cationic polyelectrolye, the cationic polyelectrolyte being present in an amount sufficient to render the pigment particles cationic; in that said adhesive is a cationic or non-ionic adhesive; and in that said particulate pigment is one which is not capable of being dispersed in water at high solids, and following vigorous mixing, in the sole presence of said cationic polyeletrolyte.

According to a second aspect of the present invention there is provided a method of coating a sheet member comprising the step of coating the sheet member with a paper coating composition in accordance with the first aspect of this invention. The coated paper may advantageously be recycled in a paper making process.

The particulate pigment used in the present invention is one which is not capable of being dispersed in water at high solids (such as greater than 60% by weight) and following vigorous mixing, (for example sufficient to dissipate at least 10kJ of energy per kg of dry pigment), in the sole presence of the cationic polyelectrolyte. This means that the pigment surface should have a neutral, or overall positive, charge. This is true of inorganic pigments such as calcium carbonate, calcium sulphate, talc and calcined kaolin clay, for example. Most preferably, the pigment is calcium carbonate, in any form, natural or synthetic. Most preferred is ground or crushed marble, but chalk, or precipitated calcium carbonate (PCC) may also be used. In this respect, it should be noted that whilst raw chalk is capable of being dispersed using a cationic polyelectrolyte in the absence of vigorous mixing, this is not true if the chalk is subject to vigorous mixing. It is believed that this is because the vigorous mixing strips off the anionic aluminosiliceous layer normally present on raw chalk. In the absence of vigorous mixing, the aluminosiliceous layer is able to confer a negative charge on the surface of the chalk particles and this enables dispersion by a cationic polyelectrolyte to be achieved.

It is preferred that the ground pigment has a particle size distribution such that at least 50% percent by weight has an equivalent spherical diameter smaller than two μm. More preferably, at least 60% percent by weight has an equivalent spherical diameter smaller than two μm.

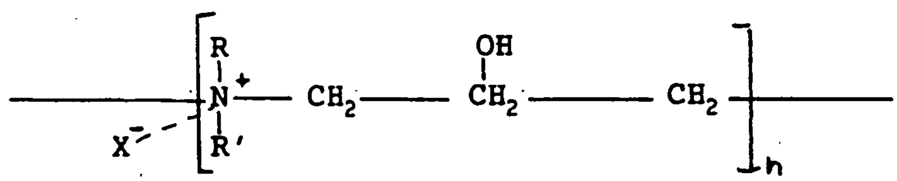
Ground marble for use in the present invention is preferably formed by crushing batches of marble in aqueous suspension in the absence of a chemical dispersing agent using a particulate grinding medium. Any agglomerates formed may be broken up by dewatering the suspension of ground marble, for example by filtration in the absence of a flocculating agent and then drying the pigment, and pulverising the dried

product in a conventional mill.

The particulate pigment is dispersed with the combination of an anionic polyelectrolyte and a cationic polyelectrolyte. Preferably, the anionic polyeletrolyte is a water-soluble vinyl polymer, an alkali metal or ammonium salt thereof or an alkali metal or ammonium salt of polysilicic acid. Most preferably, the anionic polyeletrolyte is a poly(acrylic acid), a poly(methacrylic acid), a substituted poly(acrylic acid) or a substituted poly(methacrylic acid), or an alkali metal or ammonium salt of any of these acids. The substituted poly(acrylic acid) may be a partially sulphonated polymer. An especially effective anionic polyelectrolyte is an alkali metal or ammonium salt of a copolymer of acrylic acid and a sulphonic acid derivative of acrylic acid, in which the proportion of the sulphonic acid derivative monomer is preferably from 5% to 20% of the total number of monomer units.

The number average molecular weight of the anionic polyelectrolyte is preferably at least 500, and preferably no greater than 100,000. The amount used is generally in the range of from about 0.01% to about 0.5% by weight based on the weight of dry pigment, preferably in the range of from about 0.1 to 0.2% by weight.

The cationic polyelectrolyte may be a water-soluble substituted polyolefine containing quaternary ammonium groups. The quaternary ammonium groups may be in the linear polymer chain or may be in branches of the polymer chain. The number average molecular weight of the substituted polyolefine is preferably at least 1500 and preferably no greater than 1,000,000, and is more preferably in the range of from 50,000 to 500,000. The quantity required is generally in the range of from about 0.01% to about 1.5% by weight based on the weight of dry pigment. Advantageous results have been obtained when the substituted polyolefine is a poly (diallyl di(hydrogen or lower alkyl)ammonium salt). The lower alkyl groups, which may be the same or different, may for example, have up to four carbon atoms and each is preferably methyl. The ammonium salt may be, for example, a chloride, bromide, iodide, HSO_4^-, $CH_3SO_4^-$ or nitrite. Preferably the salt is a chloride. Most preferably, the cationic polyelectrolyte is poly (diallyl dimethyl ammonium chloride). Alternatively, the water-soluble substituted polyolefin may be the product of co-polymerising epichlorohydrin and an aliphatic secondary amine, said product having the formula



in which R and R', which may be the same of different, are each hydrogen or a lower alkyl group having from one to four carbon atoms, preferably methyl or ethyl and X is Cl^-, Br^-, I^-, HSO_4^-, $CH_3SO_4^-$ or nitrite. The preferred number average molecular weight of this epichlorohydrin product is in the range of from 50,000 to 300,000.

Alternatively, the cationic polyelectrolyte may be a water-soluble organic compound having a plurality of basic groups and preferably having a number average molecular weight of at least 10,000 and preferably no greater than 1,000,000. Most preferably, the number average molecular weight is at least 50,000. These water-soluble organic compounds may be described as polyacidic organic bases, and are preferably compounds of carbon, hydrogen and nitrogen only and are free of other functional groups, such as hydroxy or carboxylic acid groups, which would increase their solubility in water and thus increase the likelihood of their being desorbed from the clay mineral in an aqueous suspension. Preferably, the organic compound is polyethyleneimine (PEI) having a number average molecular weight in the range 50,000 to 1,000,000. A further example of a water-soluble organic compound which may be employed is a polyethylene diamine which may be a copolymer of ethylene diamine with an ethylene dihalide or with formaldehyde.

The cationic polyelectrolyte is employed in an amount sufficient to render the mineral particles cationic. Experiments have shown that the zeta potential of the particles will normally be at least +20mV after treatment, typically in the range of from +30 to +40 mV and usually no greater than +50 to +60mV. These potentials have been measured using a dilute (0.02 weight %) solids suspension using a supporting electrolyte of potassium chloride (10^{-4} M) with a "Pen Kem Laser Z" meter.

The ratio of the weight of cationic polyelectrolyte to the weight of anionic polyelectrolyte used is preferably in the range of from 2:1 to 20:1, in particular when the calcium carbonate is a ground marble.

According to a third aspect of the present invention, there is provided a process for preparing a paper coating composition comprising the steps of:

(i) dispersing in aqueous suspension a particulate pigment; and

(ii) combining the dispersed aqueous suspension with an adhesive and, if necessary, adjusting the dilution such that the particulate material constitutes at least 45% by weight of the composition;

characterised in that said pigment is dispersed using a dispersing agent comprising a combination of an anionic polyelectrolyte and a cationic polyelectrolyte; in that said cationic polyelectrolyte is used in an amount sufficient to render the pigment particles cationic; in that said adhesive is a cationic or non-ionic adhesive; and in that said particulate pigment is one which is not capable of being dispersed in water at high solids, and following vigorous mixing, in the sole presence of said cationic polyeletrolyte.

In the method of the invention, it is normally the case that the raw pigment is received as a filter cake having a relatively high solids content. To this is added the dispersing agent in order to provide a dispersed high solids slurry (45-80% by weight solids) which may then be subjected to vigorous mixing. This slurry is then "made down" into a paper coating composition by dilution and addition of the required quantity of the cationic or non-ionic adhesive and other conventional paper coating composition adjuvants.

Preferably, the pigment is mixed with the anionic polyeletrolyte before mixing with the cationic polyelectrolyte. This appears to enable a more fluid suspension to be obtained at a higher solids concentration.

The aqueous dispersion of the pigment may also include other conventional paper coating composition adjuvants such as an insolubilising agent (e.g. a melamine formaldehyde resin), a lubricant such as calcium stearate and a catalyst to catalyze cross-linking of the cationic latex if present: a suitable such catalyst is sodium bicarbonate. The quantities of these adjuvants required are known to those skilled in the art.

The adhesive used in the present invention should be a non-ionic or a cationic adhesive. Such adhesives contrast with the anionic adhesives which are normally used in paper coating compositions in which the pigment is anionic. Thus, cationic guar gum and cationic starch adhesives can be used as well as cationic or non-ionic latices. Such cationic and non-ionic adhesives are readily commercially available. The particular cationic or non-ionic adhesive used will depend, for example, on the printing process to be used, e.g. offset lithography requires the adhesive to be water-insoluble. For paper to be used in an offset printing technique, the amount of adhesive should preferably be of the order of from 7 to 25% by weight, based on the weight of pigment whilst, for gravure printing paper, the adhesive should be used in an amount of 4-15% by weight, based on the weight of pigment. The precise quantity of adhesive required will depend upon the nature of the adhesive and the material being coated, but this can readily be determined by the person skilled in the art.

The suspension of the pigment for incorporation into the paper coating composition of the present invention should preferably be subjected to vigorous mixing before or after dispersion. Typically, the vigorous mixing should be sufficient to impart at least 10kJ energy per kg of pigment, and preferably no more than about 50kJ per kg. Normally, the amount of energy input will be in the range of from 18-36kJ per kg of pigment.

The coating composition may be coated on to a sheet member using normal paper coating machinery and under normal paper coating conditions. It has been found that the paper coated with a cationic composition in accordance with the present invention provides broadly similar results to that obtained with a conventional anionic system.

The coated paper of the present invention is of advantage when it is employed as "broke" or recycled paper in a paper making process. Commonly, large quantities of paper are recycled at the point of manufacture for one reason or another, and the advantages of the paper of the present invention in recycling are most important to the paper manufacturer. Thus, in accordance with a fourth aspect of the present invention, there is provided a method for recycling paper including the step of reducing paper made in accordance with the second aspect of the present invention to a fibrous recyclable state and incorporating said fibre in a paper-making composition.

Such a paper-making composition may include conventional paper-making pulp, such as a bleached sulphite pulp and, typically, the broke fibre and the pulp will be employed in a ratio of from 10:90 to 60:40.

Also included in the paper making composition will be a filler, for instance a calcium carbonate filler and also a retention aid. Since the broke fibre will include a proportion of calcium carbonate from the coating, it is possible to reduce the amount of calcium carbonate filler employed to give a total quantity of filler in the range of from 5 to 20 percent by weight of the total paper-making composition. The weight of dried broke added (fibre and filler) should preferably be in the range of from about 5 to 30 percent by weight of fibre.

It has been found that, when the broke fibre employed is derived from a coated paper in accordance with the present invention, this enables the amount of retention aid employed in the paper making composition to be reduced.

The present invention will now be illustrated by the following examples:

EXAMPLE 1

Three batches of raw crushed marble were ground in an aqueous suspension containing 30% by weight of dry solids and in the absence of chemical dispersing agent, by means of a particulate grinding medium. The duration of grinding was different in each case so as to yield three different ground products having particle size distributions such that 50%, 68% and 87% by weight, respectively, had an equivalent spherical diameter smaller than 2 µm. In each case the suspension of ground marble was dewatered by filtration in a tube pressure filter in the absence of a flocculating agent and the filter cake was dried and pulverised in a laboratory hammer mill.

Samples of each of the three ground marble powders were mixed with water and with two different dispersing agents by each of two different methods described below. The dispersing agents were:-

(E) an anionic polyelectrolyte which was a sodium polyacrylate having a number average molecular weight of 4,000; and

(F) a cationic polyelectrolyte which was a poly (diallyl dimethyl ammonium chloride) having a number average molecular weight of 50,000.

In each case the ratio of weight of (F) to the weight of (E) was 4:1 but the optimum total quantity of dispersing agents was determined for each ground marble powder and was found to differ in each case. The two methods for preparing the aqueous suspension of the marble powders were:-

(i) the powder was mixed with water containing the required quantity of (E) and after thorough mixing the required quantity of (F) was added, followed by further mixing; and

(ii) the powder was mixed with water containing the required quantities of both (E) and (F) together.

In each case the viscosity of the suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 rpm. and the percentage by weight of dry solids was determined by completely drying a known weight of the suspension and weighing the dried residue. The suspension was then diluted with a small quantity of water and further determinations of viscosity and percentage by weight of dry solids were made. A graph was plotted of viscosity against percentage by weight of dry solids and the solids concentration for a suspension having a viscosity of 500 mPa.s was determined by interpolation.

The results obtained are set forth in Table I below:-

TABLE 1

% by wt. smaller than 2 µm in marble	% by wt. based on wt. of dry marble of		% by wt. of dry solids for a viscosity of 500 mPa.s by method	
	(E)	(F)	(i)	(ii)
50	0.02	0.083	72.0	71.3
68	0.075	0.289	71.4	65.6
87	0.166	0.65	64.6	60.3

These results show that fluid suspension can be obtained at a higher solids concentration by method (i) (mixing the powder firstly with the anionic polyelectrolyte and secondly with the cationic polyelectrolyte) than by method (ii) (mixing the powder with both dispersing agents together). This effect is more marked with finely ground marble powders than with a coarser product.

EXAMPLE 2

A further batch of finely ground marble powder was prepared by the process described in Example 1, the particle size distribution of the ground product being such that 87% by weight consisted of particles having an equivalent spherical diameter smaller than 2 µm.

Samples of this marble powder were incorporated into paper coating compositions prepared according to the following recipes:-

	Ingredient	Parts by weight
Composition (a)	Marble powder Quaternary cationic acrylic latex Cationic guar gum	100 12 0.5

	Ingredients	Parts by weight
Composition (b)	Marble powder Quaternary cationic acrylic latex Cationic starch	100 8 4

Three different compositions of type (b) were prepared containing the following three different cationic starches:-

(i) a cationic starch of low degree of substitution
(ii) another cationic starch of low degree of substitution
(iii) a cationic starch of high degree of substitution

The three compositions were identified as compositions (b)(i), (b)(ii) and (b)(iii), respectively

	Ingredient	Parts by weight
Composition (c)	Marble powder Styrene butadiene rubber latex Sodium carboxymethyl cellulose	100 12 0.75

	Ingredient	Parts by weight
Composition (d)	Marble powder Styrene butadiene rubber latex Oxidised starch	100 8 4

In the case of the cationic compositions (a) and (b) an aqueous suspension of the marble powder was first prepared using as the dispersing agents 0.16% by weight, based on the weight of dry marble, of anionic dispersing agent (E) and 0.65% by weight, based on the weight of dry marble, of cationic dispersing agent (F), by the method described under (i) in Example 1 above.

In the case of the anionic compositions (c) and (d) the marble powder was treated with 0.30% by weight, based on the weight of dry marble, of dispersing agent (E) alone.

In addition there were added to each of compositions (a), (b), (c) and (d) 0.8 part by weight of a melamine formaldehyde resin, as an insolubilising agent, and 0.5 part by weight of calcium stearate. There was also added to each of the cationic compositions (a) and (b) 0.2 part by weight of sodium bicarbonate to catalyse the cross linking reaction of the cationic latex.

Each paper coating composition was diluted with water to give a high-shear viscosity as measured by a Ferranti-Shirley Viscometer at a shear rate of 12,800 s^{-1} in the range 60-70 mPa.s if possible. The high-shear viscosities and the percentage by weight of solids in the diluted compositions are set forth in Table II below.

Each composition was coated on to a lightweight offset base paper of substance weight 48 $g.m^{-2}$ by means of a laboratory paper coating machine of the type described in British Patent Specification No. 1032536. The coated paper samples were then supercalendered under a pressure of 1000 psi (6.89 MPa) and a temperature of 65 °C with 10 passes through the nip of the calender rolls at a speed of $36 m.min^{-1}$.

Each sample of calendered, coated paper was tested for gloss by the TAPPI Standard method, for smoothness by the Parker Print Surf at 98N (10 Kgf.), for percentage reflectance to light of wavelength 457nm and for percentage opacity. In each case the determinations of gloss, smoothness, % reflectance and % opacity were obtained by coating samples of paper at a range of different coat weights, measuring these quantities for each coat weight, plotting a graph of the quantity against coat weight and interpolating

to find the value of quantity for a coat weight of $8 g.m^{-2}$. The results are set forth in Table II below:-

TABLE II

Composition	% by wt. of dry solids	High shear viscosity (mPa.s)	Gloss (TAPPI units)	Smoothness	% reflectance to light of 457nm. wavelength	% opacity
(a)	62.0	62	45	0.72	78.1	90.1
(b)(i)	60.6	66	45	1.05	78.4	90.4
(b)(ii)	61.2	70	43	0.68	78.4	89.8
(b)(iii)	59.4	72	38	0.71	78.4	90.1
(c)	65.8	73	46	0.67	78.1	90.1
(d)	64.9	104	39	0.76	77.8	89.7

When the results for cationic composition (a) are compared with those for the corresponding anionic composition (c), and the results for the cationic compositions of type (b) are compared with those for the corresponding anionic composition (d), it will be noted that the coated paper properties for a cationic system in accordance with the invention are broadly similar to those obtained with a conventional anionic system.

Samples of paper coated with the above coating compositions were used as recycled paper or "broke" in a paper making process. Bleached sulphite pulp was beaten in accordance with TAPPI Standard T200 to a degree of freeness of 45 SR or 270 Canadian Standard Freeness and paper making compositions were prepared consisting of suspensions in water of the following ingredients:-

Ingredient	**Parts of weight**
Bleached sulphite pulp	70
Broke fibre	30
Calcium carbonate filler	50
Polyacrylamide retention aid	0.03

The calcium carbonate filler had a particle size distribution such that 43% by weight consisted of particles having an equivalent spherical diameter smaller than 2 μm. Since the broke contained about 20% by weight of inorganic filler material the quantity of fresh calcium carbonate filler added was reduced to give a total quantity of filler of 50 parts by weight. Similarly the weight of dry broke added (fibre + filler) was such as to provide 30 parts by weight of fibre.

The retention of the calcium carbonate filler in paper prepared from compositions containing broke which had been coated with each of the coating compositions (a), (b)(ii), (c) and (d) above was measured by means of a retention jar with the stirrer set at speed 5 (1050 rpm) and a stirring duration of 30 seconds. As a comparison the retention of the same calcium carbonate filler in a paper making composition containing no broke was also measured. The results are set forth in Table III below:-

TABLE III

Broke containing coating composition	% by wt. retention of calcium carbonate
None	74.3
(a)	83.9
(b)(ii)	79.2
(c)	49.8
(d)	46.2

These results show that although the incorporation into paper making composition of broke which has been coated with an anionic composition (c) and (d) reduces the retention of a calcium carbonate filler as compared with a paper making composition which contains no broke, the incorporation of broke coated with

a cationic composition actually improves the retention of the filler.

EXAMPLE 3

A batch of raw crushed marble was ground by the method described in Example 1 above to give a ground product having a particle size distribution such that 60% by weight consisted of particles having an equivalent spherical diameter smaller then 2 µm. The suspension of ground marble was dewatered by means of a centrifuge and the centrifuge cake which contained 68% by weight of dry solids was used in the following experiments.

Samples of the centrifuge cake of ground marble were mixed first with an anionic dispersing agent, and then, after thorough mixing, with a cationic dispersing agent. In each case a predetermined quantity of the anionic dispersing agent was used, but, for the cationic dispersing agent, a small quantity of the dispersing agent was first added, the suspension was vigorously mixed for 1 minute, and the viscosity of the suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 rpm. The amount of dispersing agent and the viscosity were recorded and a further small quantity of the dispersing agent was added and the procedure repeated. Further small increments of the dispersing agent were added until the viscosity of the suspension reached a minimum, at which point the total amount of the cationic dispersing agent which had been added was regarded as the optimum.

The dispersing agents were:-

(G) an anionic polyelectrolyte which was a sodium polyacrylate having a number average molecular weight of 70,000

(H) sodium silicate which is a sodium salt of a polysilicic acid and acts as an anionic dispersing agent;

(I) a cationic polyelectrolyte which was a poly (diallyl dimethyl ammonium chloride) having a number average molecular weight of 50,000.

(J) a cationic polyelectrolyte which was a polyethyleneimine.

When dispersing agent (J) was used it was also necessary to add sufficient sulphuric acid to adjust the pH to 7.8 since polyethyleneimines are sensitive to pH and do not act efficiently as dispersing agents at pH values greater than 8.

As a comparison one sample of the centrifuge cake was treated with dispersing agent (J) at pH 7.8 alone, no anionic dispersing agent being used.

For each combination of dispersing agents the percentage by weight of dry marble in the suspension, the minimum viscosity of the suspension and the quantities of anionic and cationic dispersing agent were recorded, and the results are set forth in Table IV below:-

TABLE IV

Anionic dispersing agent	Amount used (% by wt.)	Cationic dispersing agent	Amount used (% by wt.)	% by wt. of dry solids	Minimum viscosity (mPa.s)
G	0.10	I	0.48	67.2	3000
G	0.10	J	0.40	67.5	252
H	0.16	J	0.39	65.4	224
none	-	J	0.37	67.1	>10,000

These results show that, in general, lower viscosities are obtainable with polyethyleneimine as the cationic dispersing agent, rather than with poly (diallyl dimethyl ammonium chloride), but the use of the cationic dispersing agent must be preceded by the addition of an anionic dispersing agent.

EXAMPLE 4

A batch of marble flour having a particle size distribution such that substantially all of the particles passed through a No. 300 mesh British Standard sieve (nominal aperture 53 µm) was subjected to attrition grinding in a concentrated, deflocculated aqueous suspension, the quantities of marble flour, water and grinding sand being:-

615g marble flour

330g water + anionic and cationic dispersing agents

1500g sand

The grain size of the sand was smaller than No. 18 mesh British Standard sieve (nominal aperture

0.850mm) and larger than No. 30 mesh British Standard sieve (nominal aperture 0.500mm). The anionic dispersing agent used was (E) and the cationic dispersing agent was (F), both as described in Example 1 above. Portions of marble flour were ground using different total quantities of (E) and (F) but in each case the weight ratio of (F):(E) was 4:1. In each case the grinding was continued for a time sufficient to dissipate in the suspension 396 kJ of energy per kg of dry marble and in each case the product had a particle size distribution such that about 50% by weight consisted of particles having an equivalent spherical diameter smaller than 2 µm. On completion of grinding the suspension of ground marble was separated from the sand and the viscosity of the suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 rpm. The suspension was then diluted with a small quantity of water and the viscosity was measured again. The percentage by weight of dry marble in the suspension was also determined by drying a known small weight of the suspension and weighing the dried residue. The steps of diluting with water and measuring the viscosity and percentage by weight of dry marble were repeated several times. A graph was drawn of viscosity against percentage by weight of dry marble and the percentage by weight of dry marble in the suspension which had a viscosity of 500 mPa.s was found by interpolation. The results are set forth in Table V below:-

TABLE V

% by wt. of (E)	% by wt. of (F)	Total % by wt. of dispersing agents	% by wt. of dry marble for a viscosity of 500 mPa.s
0.05	0.20	0.25	63.9
0.06	0.24	0.30	64.5
0.07	0.28	0.35	65.0

EXAMPLE 5

Further batches of the same marble flour as was used in Example 4 were ground by the method described in Example 4, there being used as the anionic dispersing agent 0.07% by weight, based on the weight of dry marble, of (E), and as the cationic dispersing agent 0.28% by weight, based on the weight of dry marble, of one of a selection of poly (diallyl dimethyl ammonium chloride) polyelectrolytes of different molecular weights. In each case the percentage by weight of dry marble in a suspension having a viscosity of 500 mPa.s was measured as described in Example 4 above and the results are set forth in Table VI below:-

TABLE VI

Number average molecular weight of cationic dispersing agent	% by wt. of dry marble for a viscosity of 500 mPa.s
9,500	58.4
26,000	61.8
50,000	65.0
71,500	64.9

These results show that the poly (diallyl dimethyl ammonium chloride) should have a number average molecular weight of at least 50,000 if a marble suspension of acceptable fluidity is to be obtained.

EXAMPLE 6

A batch of raw crushed marble was ground by the method described in Example 1 to give a ground product having a particle size distribution such that 60% by weight consisted of particles having an equivalent spherical diameter smaller than 2 µm. The suspension of ground marble was dewatered by means of centrifuge and the centrifuge cake which contained 73% by weight of dry solids was used in the following experiments:

Samples of the ground marble centrifuge cake were first mixed with 0.1% by weight, based on the

weight of dry marble, of anionic dispersing agent G as described in Example 3 (i.e. a sodium polyacrylate having a number average molecular weight of 70,000). After thorough mixing there was added to each sample of aqueous suspension of anionically dispersed ground marble a quantity of one of the four following cationic dispersing agents:-

(I) a cationic polyelectrolyte which was a poly(diallyl dimethyl ammonium chloride) having a number average molecular weight of 50,000 - 100,000;

(J) a cationic polyelectrolyte which was a polyethyleimine;

(K) a polyethyleneimine of number average molecular weight lower than that of (J);

(L) a polyethyleneimine of number average molecular weight lower than that of (K).

The quantity of each cationic dispersing agent was that which was found by experiment to give the lowest viscosity for a suspension of given solids content. For dispersing agent (I) this quantity was found to be 0.45% by weight, based on the weight of dry marble, and for dispersing agents (J), (K) and (L) the quantity was found to be 0.40% by weight, based on the weight of dry marble.

In the case of the polyethyleneimine dispersing agents (J), (K) and (L) there was also added sufficient sulphuric acid to adjust the pH to 7.8. In each case the viscosity of the suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 rpm and the percentage by weight of dry solids in the suspension was determined by completely drying a known weight of the suspension and weighing the dried residue. The suspension was then diluted with a small quantity of water and further determinations of viscosity and percentage by weight of dry solids were made. The procedure of diluting the suspension and measuring the viscosity and percentage by weight of dry solids was repeated two or three times and a graph was plotted of viscosity against percentage by weight of dry solids. The solids concentration for a suspension having a viscosity of 300 mPa.s was determined by interplotation and the results are set forth in Table VII:-

TABLE VII

Cationic dispersing agent	% by weight of dry marble for a viscosity of 300 mPa.s
I	61.0
J	68.5
K	71.8
L	73.0

EXAMPLE 7

A batch of raw crushed marble was ground in an aqueous suspension containing 30% by weight of dry solids and in the absence of chemical dispersing agent, by means of a particulate grinding medium to yield a ground calcium carbonate product of paper coating grade having a particle size distribution such that 90% by weight of the particles had an equivalent spherical diameter smaller than 2 μm. The suspension of ground marble was dewatered by filtration in the absence of a flocculating agent and the filter cake was dried and pulverised in a laboratory hammer mill.

Samples of the finely ground marble powder were mixed with water to form a suspension containing 60% by weight of dry solids and varying quantities of an anionic and of a cationic dispersing agent. The anionic dispersing agent was a sodium polyacrylate dispersing agent having a number average molecular weight of 4000 and the cationic dispersing agent was a poly (diallyl dimethyl ammonium chloride) having a number average molecular weight of about 50,000.

In each experiment the anionic dispersing agent was added first to the suspension of ground marble and the mixture stirred by 9,400 revolutions of an impeller rotating at 1,420 rpm. The cationic dispersing agent was then added and the mixing procedure was repeated. The viscosity was measured immediately on completion of the second mixing procedure by means of a Brookfield Viscometer.

The results obtained are set forth in Table VIII below:

Table VIII

Total % by wt. of mixed dispersing agents	% by wt. of anionic dispersing agent	% by wt. of cationic dispersing agent	Wt. ratio cationic : anionic	Viscosity (mPa.s)
0.416	0.053	0.363	6.9	10,000
0.642	0.082	0.560	6.9	4,600
0.850	0.108	0.742	6.9	106
1.03	0.131	0.899	6.9	82
1.29	0.164	1.13	6.9	78
2.07	0.263	1.81	6.9	480
0.348	0.070	0.278	4.0	9,400
0.504	0.101	0.403	4.0	3,600
0.616	0.123	0.493	4.0	60
0.800	0.160	0.640	4.0	74
1.02	0.204	0.816	4.0	576
1.28	0.256	1.02	4.0	2,400
0.364	0.102	0.262	2.6	3,600
0.570	0.159	0.411	2.6	1,800
0.732	0.205	0.527	2.6	3,400
0.910	0.254	0.656	2.6	4,350
1.05	0.294	0.756	2.6	4,650
1.60	0.447	1.15	2.6	4,150
0.145	0.053	0.092	1.7	10,000
0.273	0.100	0.173	1.7	6,150
0.351	0.129	0.222	1.7	3,360
0.434	0.160	0.274	1.7	7,600
0.541	0.199	0.342	1.7	7,900
0.790	0.291	0.499	1.7	5,900
1.26	0.464	0.796	1.7	6,000

These results show that the optimum dispersion was obtained when the ratio of the weight of cationic dispersing agent to the weight of anionic dispersing agent was about 4:1. When the ratio was increased to 6.9:1 it was still possible to obtain a very fluid suspension but at the expense of a slightly higher dose of mixed dispersing agents.

EXAMPLE 8

A batch of raw crushed marble was ground in an aqueous suspension containing 30% of dry solids and in the absence of chemical dispersing agents by means of a particulate grinding medium to yield a ground product having a particle size distribution such that 78% by weight of the particles had an equivalent spherical diameter smaller than 2 µm. The suspension of ground marble was dewatered in the absence of a flocculating agent on a vacuum drum filter to a dry solids content of 64% by weight. Some of the filter cake

thus formed was thermally dried and mixed back with the moist filter cake to give a mixture having a dry solids content of 70% by weight.

This mixture was divided into three portions to be treated with cationic poly(diallyl dimethyl ammonium chloride) dispersing agents having three different number average molecular weights. Each of the three portions were further subdivided into three smaller portions which were treated with different doses of anionic dispersing agent (E) as described in Example 1.

In each case the anionic dispersing agent was added first to the cake of ground marble and well mixed therewith, and the cationic dispersing agent was then added and mixed in. The dose of the cationic dispersing agent used was in each case about 3.5 times the dose of the anionic dispersing agent.

In each case the viscosity of the resultant suspension was measured by means of a Brookfield Viscometer at a spindle speed of 100 rpm and the percentage by weight of dry solids was determined by completely drying a known weight of the suspension and weighing the dried residue. The suspension was then diluted with a small quantity of water and further determinations of viscosity and percentage by weight of dry solids were made. A graph was plotted of viscosity against percentage by weight of dry solids and the solids content for a suspension having a viscosity of 300 mPa.s was determined by interpolation.

The results obtained are set forth in Table IX below:-

Table IX

Mol. wt. of cationic dispersing agent	% by wt. of anionic dispersing agent	% by wt. of cationic dispersing agent	% by wt. of dry solids of a viscosity of 300 mPa.s
100,000	0.080	0.265	64.1
100,000	0.108	0.370	65.4
100,000	0.124	0.450	64.7
200,000	0.074	0.260	64.7
200,000	0.100	0.360	68.1
200,000	0.125	0.450	67.1
500,000	0.075	0.260	67.9
500,000	0.100	0.360	68.4
500,000	0.125	0.450	67.6

The results show that slightly more fluid suspensions for a given solids content were obtained when the cationic dispersing agent having a number average molecular weight of 500,000 was used.

Claims

1. An aqueous paper coating composition which comprises (i) at least 45% by weight of a particulate inorganic pigment dispersed with a dispersing agent and (ii) an adhesive; characterised in that said dispersing agent comprises an anionic polyelectrolyte and a cationic polyelectrolye, the cationic polyelectrolyte being present in an amount sufficient to render the pigment particles cationic; in that said adhesive is a cationic or non-ionic adhesive; and in that said particulate pigment is one which is not capable of being dispersed in water at high solids, and following vigorous mixing, in the sole presence of said cationic polyeletrolyte.

2. A paper coating composition according to claim 1, wherein the pigment is selected from calcium carbonate, calcium sulphate, talc or a calcined kaolin clay.

3. A paper coating composition according to claim 1, wherein the pigment is a calcium carbonate pigment.

4. A paper coating composition according to any preceding claim, wherein the number average molecular weight of the anionic polyelectrolyte is in the range of from 500 to 100,000.

5. A paper coating composition according to any preceding claim, wherein the anionic polyelectrolyte is employed in an amount in the range of from 0.01% to 0.5% by weight based on the weight of dry pigment.

6. A paper coating composition according to any preceding claim, wherein the cationic polyelectrolyte is a water-soluble substituted polyolefine containing quaternary ammonium groups.

7. A paper coating composition according to claim 6, wherein the number average molecular weight of the substituted polyolefine is in the range of from 1500 to 1,000,000.

8. A paper coating composition according to claim 6 or 7, wherein the amount of cationic polyelectrolyte employed is in the range of from 0.01% to 1.5% by weight based on the weight of dry pigment.

9. A paper coating composition according to any one of claims 1 to 5, wherein the cationic polyelectrolyte is a water-soluble organic compound having a plurality of basic groups and a number average molecular weight in the range of from 10,000 to 1,000,000.

10. A paper coating composition according to claim 9, wherein the organic compound is polyethyleneimine having a number average molecular weight in the range of from 50,000 to 1,000,000.

11. A paper coating composition according to any preceding claim, wherein the ratio of the weight of cationic polyelectrolyte to the weight of anionic polyelectrolyte is in the range of from 2:1 to 20:1.

12. A process for preparing a paper coating composition comprising the steps of:
(i) dispersing in aqueous suspension a particulate pigment; and
(ii) combining the dispersed aqueous suspension with an adhesive and, if necessary, adjusting the dilution such that the particulate material constitutes at least 45% by weight of the composition;
characterised in that said pigment is dispersed using a dispersing agent comprising a combination of an anionic polyelectrolyte and a cationic polyelectrolyte; in that said cationic polyelectrolyte is used in an amount sufficient to render the pigment particles cationic; in that said adhesive is a cationic or non-ionic adhesive; and in that said particulate pigment is one which is not capable of being dispersed in water at high solids, and following vigorous mixing, in the sole presence of said cationic polyeletrolyte.

13. A process according to claim 12, wherein the pigment is selected from calcium carbonate, calcium sulphate, talc or calcined kaolin clay.

14. A process according to claim 13, wherein the pigment is a calcium carbonate pigment

15. A process according to claim 12, 13 or 14, wherein the pigment is mixed with the anionic polyelectrolyte before mixing with the cationic polyelectrolyte.

16. A method of coating paper comprising the step of coating the paper with a paper coating composition in accordance with any one of claims 1 to 11.

17. A method for recycling paper including the step of reducing a coated paper made by the method of Claim 16 to a fibrous recyclable state and incorporating said fibre in a paper-making composition.

Patentansprüche

1. Wäßriges Papierbeschichtungsmittel, umfassend (i) mindestens 45 Gew.% eines mit einem Dispersionsmittel dispergierten partikelförmigen anorganischen Pigments und (ii) einen Klebstoff, dadurch gekennzeichnet, daß das Dispersionsmittel einen anionischen Polyelektrolyt und einen kationischen Polyelektrolyt umfaßt, wobei der kationische Polyelektrolyt in einer ausreichenden Menge vorhanden ist, damit die Pigmentpartikel kationisch werden; daß der Klebstoff ein kationischer oder nichtionischer Klebstoff ist; und daß das partikelförmige Pigment ein Pigment ist, das bei hohem Feststoffgehalt und nach kräftigem Mischen in der alleinigen Gegenwart des kationischen Polyelektrolyts nicht in Wasser dispergiert werden kann.

2. Papierbeschichtungsmittel nach Anspruch 1, wobei das Pigment aus Calciumcarbonat, Calciumsulfat, Talkum oder gebranntem Kaolinton ausgewählt ist.

3. Papierbeschichtungsmittel nach Anspruch 1, wobei das Pigment Calciumcarbonatpigment ist.

4. Papierbeschichtungsmittel nach einem der vorstehenden Ansprüche, wobei das Zahlenmittel des Molekulargewichts des anionischen Polyelektrolyts im Bereich von 500 bis 100.000 liegt.

5. Papierbeschichtungsmittel nach einem der vorstehenden Ansprüche, wobei der anionische Polyelektrolyt in einer Menge im Bereich von 0,01 bis 0,5 Gew.% des trockenen Pigments verwendet wird.

6. Papierbeschichtungsmittel nach einem der vorstehenden Ansprüche, wobei der kationische Polyelektrolyt ein wasserlösliches substituiertes Polyolefin ist, das quaternäre Ammoniumgruppen enthält.

7. Papierbeschichtungsmittel nach Anspruch 6, wobei das Zahlenmittel des Molekulargewichts des substituierten Polyolefins im Bereich von 1.500 bis 1.000.000 liegt.

8. Papierbeschichtungsmittel nach Anspruch 6 oder 7, wobei die verwendete Menge des kationischen Polyelektrolyts im Bereich von 0,01 bis 1,5 Gew.% des trockenen Pigments liegt.

9. Papierbeschichtungsmittel nach einem der Ansprüche 1 bis 5, wobei der kationische Elektrolyt eine wasserlösliche organische Verbindung mit einer Anzahl basischer Gruppen und einem Zahlenmittel des Molekulargewichts im Bereich von 10.000 bis 1.000.000 ist.

10. Papierbeschichtungsmittel nach Anspruch 9, wobei die organische Verbindung Polyethylenimin mit einem Zahlenmittel des Molekulargewichts im Bereich von 50.000 bis 1.000.000.

11. Papierbeschichtungsmittel nach einem der vorstehenden Ansprüche, wobei das Gewichtsverhältnis des kationischen Polyelektrolyts zum anionischen Polyelektrolyt im Bereich von 2:1 bis 20:1 liegt.

12. Verfahren zur Herstellung eines Papierbeschichtungsmittels, umfassend die Schritte:
(i) Dispergieren eines partikelförmigen Pigments in einer wäßrigen Suspension; und
(ii) Mischen der dispergierten wäßrigen Suspension mit einem Klebstoff und bei Bedarf Einstellen der Verdünnung, so daß das partikelförmige Material mindestens 45 Gew.% der Zusammensetzung bildet;
dadurch gekennzeichnet, daß das Pigment mit einem Dispersionsmittel dispergiert wird, das eine Kombination aus einem anionischen Polyelektrolyt und einem kationischen Polyelektrolyt umfaßt; daß der kationische Polyelektrolyt in einer ausreichenden Menge verwendet wird, damit die Pigmentpartikel kationisch werden; daß der Klebstoff ein kationischer oder nichtionischer Klebstoff ist; und daß das partikelförmige Pigment ein Pigment ist, das bei hohem Feststoffgehalt und nach kräftigem Mischen in alleiniger Gegenwart des kationischen Polyelektrolyts nicht in Wasser dispergiert werden kann.

13. Verfahren nach Anspruch 12, wobei das Pigment aus Calciumcarbonat, Calciumsulfat, Talkum oder gebranntem Kaolinton ausgewählt ist.

14. Verfahren nach Anspruch 13, wobei das Pigment Calciumcarbonatpigment ist.

15. Verfahren nach Anspruch 12, 13 oder 14, wobei das Pigment vor dem Mischen mit dem kationischen Polyelektrolyt mit dem anionischen Polyelektrolyt gemischt wird.

16. Verfahren zum Beschichten von Papier, umfassend den Schritt des Beschichtens des Papiers mit einem Papierbeschichtungsmittel nach einem der Ansprüche 1 bis 11.

17. Verfahren zur Wiederverwertung von Papier, umfassend den Schritt des Zerkleinerns von beschichtetem Papier, das nach dem Verfahren nach Anspruch 16 hergestellt wurde, zu einem fasrigen wiederverwertbaren Zustand und des Einführens der Fasern in eine Masse zur Papierherstellung.

Revendications

1. Composition aqueuse d'enduit de couchage pour papier qui comprend (i) au moins 45% en poids d'un pigment minéral particulaire dispersé avec un agent dispersant et (ii) un adhésif; caractérisée en ce que

ledit agent dispersant comprend un polyélectrolyte anionique et un polyélectrolyte cationique, le polyélectrolyte cationique étant présent en quantité suffisante pour rendre les particules de pigment cationiques; en ce que ledit adhésif est un adhésif cationique ou non ionique; et en ce que ledit pigment particulaire est un pigment qui ne peut pas être dispersé dans l'eau à forte teneur de solides, et à la suite d'un mélange énergique, en la seule présence dudit polyélectrolyte cationique.

2. Composition d'enduit de couchage pour papier selon la revendication 1, dans laquelle le pigment est sélectionné parmi le carbonate de calcium, le sulfate de calcium, le talc ou une argile de kaolin calcinée.

3. Composition d'enduit de couchage pour papier selon la revendication 1, dans laquelle le pigment est un pigment de carbonate de calcium.

4. Composition d'enduit de couchage pour papier selon l'une quelconque des revendications précédentes, dans laquelle la masse moléculaire en nombre du polyélectrolyte anionique est comprise entre 500 et 100 000.

5. Composition d'enduit de couchage pour papier selon l'une quelconque des revendications précédentes, dans laquelle le polyélectrolyte anionique est employé en une quantité comprise entre 0,01% et 0,5% en poids par rapport au poids de pigment sec.

6. Composition d'enduit de couchage pour papier selon l'une quelconque des revendications précédentes, dans laquelle le polyélectrolyte cationique est une polyoléfine substituée hydrosoluble contenant des groupes d'ammonium quaternaire.

7. Composition d'enduit de couchage pour papier selon la revendication 6, dans laquelle la masse moléculaire en nombre de la polyoléfine substituée est comprise entre 1 500 et 1 000 000.

8. Composition d'enduit de couchage pour papier selon la revendication 6 ou 7, dans laquelle la quantité de polyélectrolyte cationique employée est comprise entre 0,01% et 1,5% en poids par rapport au poids de pigment sec.

9. Composition d'enduit de couchage pour papier selon l'une quelconque des revendications 1 à 5, dans laquelle le polyélectrolyte cationique est un composé organique hydrosoluble présentant une pluralité de groupes basiques et une masse moléculaire en nombre comprise entre 10 000 et 1 000 000.

10. Composition d'enduit de couchage pour papier selon la revendication 9, dans laquelle le composé organique est un polyéthylèneimine présentant une masse moléculaire en nombre comprise entre 50 000 et 1 000 000.

11. Composition d'enduit de couchage pour papier selon l'une quelconque des revendications précédentes, dans laquelle le rapport du poids du polyélectrolyte cationique par rapport au poids du polyélectrolyte anionique est compris entre 2:1 et 20:1.

12. Procédé pour préparer une composition d'enduit de couchage pour papier comprenant les étapes consistant à:

(i) disperser en suspension aqueuse un pigment particulaire; et

(ii) combiner la suspension aqueuse dispersée avec un adhésif et, si nécessaire, ajuster la dilution de sorte que le matériau particulaire constitue au moins 45% en poids de la composition;

caractérisé en ce que ledit pigment est dispersé à l'aide d'un agent dispersant comprenant une combinaison d'un polyélectrolyte anionique et d'un polyélectrolyte cationique; en ce que ledit polyélectrolyte cationique est utilisé en quantité suffisante pour rendre les particules de pigment cationiques; en ce que ledit adhésif est un adhésif cationique ou non ionique; et en ce que ledit pigment particulaire est un pigment qui ne peut pas être dispersé dans l'eau à forte teneur de solides, et à la suite d'un mélange énergique, en la seule présence dudit polyélectrolyte cationique.

13. Procédé selon la revendication 12, dans lequel le pigment est sélectionné parmi le carbonate de calcium, le sulfate de calcium, le talc ou une argile de kaolin calcinée.

14. Procédé selon la revendication 13, dans lequel le pigment est un pigment de carbonate de calcium.

15. Procédé selon la revendication 12, 13 ou 14, dans lequel le pigment est mélangé avec le polyélectrolyte anionique avant d'être mélangé avec le polyélectrolyte cationique.

16. Procédé de couchage de papier comprenant l'étape consistant à coucher le papier avec une composition d'enduit de couchage pour papier selon l'une quelconque des revendications 1 à 11.

17. Procédé de recyclage de papier comportant l'étape consistant à réduire un papier couché fabriqué suivant le procédé de la revendication 16 à un état fibreux recyclable et à incorporer lesdites fibres dans une composition de pâte à papier.